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CRYSTAL STRUCTURE OF THE $YNi_{0.83}Ga_{1.17}$ AND $YNiIn_{0.15}Ga_{0.85}$ COMPOUNDS

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Crystal structure of the $YNi_{0.83}Ga_{1.17}$ (KHg_2, Imma, a = 0.43006(4), b = 0.69108(6), c = 0.73371(6) nm, R_1 = 0.0315, wR_2 = 0.0635) and $YNiIn_{0.15}Ga_{0.85}$ (HoNiGa, Pnma, a = 0.69313(5), b = 0.43225(7), c = 0.74315(9) nm, R_1 = 0.0777, wR_2 = 0.0658) compounds were determined from the single crystal X-ray diffraction data. Stacking of trigonal prisms in the structures were analyzed and briefly discussed.

Keywords: gallium, indium, single crystal, crystal structure.

Introduction

Investigations of quaternary systems with rare-earths metals, transition metals and indium are made in order to find new phases with their further use as functional materials. Effects of the indium substitution by another *p*-elements (Al, Ga, Ge, Sb) for ternary compounds R_2T_2In, RCu_2In and $RTIn$ (R = rare-earth metals, T = Ni, Cu) were studied [1–9]. The relationship between the magnetic properties and the electronic structure of intermetallics with a ZrNiAl-type structure were analyzed by the authors [10]. The dependence of the magnetic and electrical properties on the crystal structure of the compounds of *RTX* composition is described in [11]. The magnetic and electrical properties of intermetallic compounds can be influenced by the formation of solid solutions. The influence of the substitution of U by Y, Fe or Co in UNiAl leads to a rapid disappearance of long range magnetic order, however, the strong magnetic uniaxial anisotropy (characteristic for UNiAl) persists [12]. Chemical substitution of indium (*p*-element) by magnesium (*s*-element) destroys the long range magnetic ordering for solid solution $CeAuIn_{1-x}Mg_x$ [13]. Substitution of transition metal in solid solution $TbNi_{1-x}Cu_xAl$ leads to similar effects [14]. The change in the magnetic properties is observed for $Tb_{1-x}Y_xNiIn$ [15], $TbNi_{1-x}Au_xIn$ [16]. In this paper we present the results of the crystal structure determination of the phases in solid solutions $YNiIn_{1-x}Ga_x$ [5]. We synthesized

single crystals from alloys with different compositions. The crystal structures of YNiGa and YNiIn compounds were studied by X-ray powder diffraction [17–20].

Experimental details

Starting materials for the synthesis of the YNiGa and $YNiIn_{0.2}Ga_{0.8}$ samples were pieces of yttrium (Ventron), nickel wire (ONYXMET), indium tear drops (Johnson Matthey) and gallium lumps (Johnson Matthey), all with stated purities better than 99.9 %. The mixtures were arc-melted under an argon atmosphere and the buttons were re-melted three times to ensure homogeneity. The weight loss after the re-melting procedures was always smaller than 1 %. A special heat treatment was used for crystal growth. Arc-melted alloys with compositions YNiGa and $YNiIn_{0.2}Ga_{0.8}$ were placed in small tantalum tubes and arc-welded under an argon pressure of about 600 mbar. The tube was enclosed in an evacuated silica ampoule and the sample was heated in a Naberterm HTCT 01/16 furnace. At first samples were heated to 1100 °C during 6 hours and held at that temperature for 2 h, cooled at a rate of 3 K/h to 900 °C and held at that temperature for 6 h. Finally, the samples were cooled to room temperature within 20 h. Irregularly shaped crystal fragments were selected from the crushed samples and were investigated by Laue photographs (RKV-86 camera, white molybdenum radiation) in order to check the quality for intensity data collection. Intensity data were collected at room temperature by use of a Stoe IPDS II diffractometer (graphite monochromatized Mo *K*α radiation; oscillation mode). The structure was solved and refined with programs from the JANA 2006 [21]. The refined compositions were confirmed by the results of the EDX analysis (Zeiss EVO MA10 scanning electron microscope). The experimentally determined elements ratio for the $YNi_{0.83}Ga_{1.17}$: 35(2) at. % Y, 28(2) at. % Ni, 37(2) at. % Ga and for the $YNiIn_{0.15}Ga_{0.85}$: 36(2) at. % Y, 31(2) at. % Ni, 27(2) at. % Ga, 6(2) at. % In and are in good agreement with the refined compositions.

Results and discussion

The single crystals of the $YNi_{0.83}Ga_{1.17}$ compounds were obtained from YNiGa sample and were refined in KHg_2-type structure. This structure has two crystallographic sites 4*e* and 8*h*. Yttrium atoms occupy 4*e* site and 8*h* Wyckoff position is occupied by Ni/Ga mixture. $YNiIn_{0.15}Ga_{0.85}$ compound crystallizes in HoNiGa-type structure. All positions are fully occupied: two 4*c* sites by Y and Ni atoms, and one 4*c* site is occupied by a mixture of In/Ga atoms. Crystallographic data and the structure refinements details are listed in Table 1. Atomic coordinates and anisotropic displacement parameters in the structures are listed in Table 2. Interatomic distances in the structures are listed in Table 3. The shortest interatomic distances in the $YNi_{0.83}Ga_{1.17}$ structure occur between the sites of mixture Ni/Ga atoms, ranging from 0.249 to 0.267 nm, all slightly longer than the sum of atomic radii 0.247 nm [22]. The shortest interatomic distances in the $YNiIn_{0.15}Ga_{0.85}$ structure occur for Ni–In/Ga (0.252–0.269 nm) and Y–Ni (0.290–0.299 nm).

$YNi_{0.83}Ga_{1.17}$ and $YNiIn_{0.15}Ga_{0.85}$ compounds belong to the class of structures with trigonal-prismatic coordination of small size atoms [23]. Trigonal prisms in the structures of compounds in the $YNiIn_{1-x}Ga_x$ system are shown in Fig. 1.

Table 1

Crystallographic data and structure refinement of $YNi_{0.83}Ga_{1.17}$ and $YNiIn_{0.15}Ga_{0.85}$

Formula	$YNi_{0.83(5)}Ga_{1.17(5)}$	$YNiIn_{0.15(2)}Ga_{0.85(2)}$
Space group, Z	*Imma,* 4	*Pnma*, 4
Structure type	KHg_2	HoNiGa
Pearson symbol	*oI*12	*oP*12
Lattice parameters, nm	*a* = 0.43006(4) *b* = 0.69108(6) *c* = 0.73371(6) *V* = 0.21806(3)	*a* = 0.69313(5) *b* = 0.43225(7) *c* = 0.74315(9) *V* = 0.22265(5)
Radiation; λ, nm	Mo *Kα*; 0.071073	Mo *Kα*; 0.071073
Temperature, K	293	293
Density calc., g/cm^3	6.6755	6.6902
Absorption coeff. nm$^{-1}\cdot 10^6$	47.342	45.489
F(000)	392	401
θ range	4.05-34.95	4.02-34.81
hkl range	±6, ±10, ±11	±10, ±6, ±11
No. of reflections	2669	516
Independent reflections/ parameters/R_{int}	274/13/0.0384	325/21/0.661
Reflections with $I > 2\sigma(I)$/ R_σ	245/0.0092	325/0.393
Goodness-of-fit F^2	2.32	1.30
R_1/wR_2 for $I > 2\sigma(I)$	0.0259/0.0628	0.0309/0.0532
R_1/wR_2 for all data	0.0315/0.0635	0.0777/0.0658
highest/lowers Δρ, e Å^{-3}	1.53/-1.15	1.62/-2.10

Table 2

Atomic coordinates and anisotropic displacement parameters in the structures of $YNi_{0.83}Ga_{1.17}$ and $YNiIn_{0.15}Ga_{0.85}$

Atom	Wyckoff site	*x*	*y*	*z*	$U_{eq.}\cdot 10^2$, nm^2
$YNi_{0.83}Ga_{1.17}$					
Y	4*e*	0	1/4	0.5496(1)	0.0135(2)
*M**	8*h*	0	0.0567(1)	0.1650(1)	0.0143(2)
Atom		U_{11}	U_{22}	U_{33}	U_{23}
Y		0.0132(3)	0.0155(4)	0.0119(3)	0
*M**		0.0110(3)	0.0186(4)	0.0132(3)	-0.0038(2)
$YNiIn_{0.15}Ga_{0.85}$					
Y	4*c*	0.0133(2)	1/4	0.8014(1)	0.0142(2)
Ni	4*c*	0.2914(2)	1/4	0.0925(2)	0.0156(4)
*M***	4*c*	0.6798(2)	1/4	0.0791(1)	0.0136(3)
Atom		U_{11}	U_{22}	U_{33}	U_{13}
Y		0.0122(5)	0.0138(3)	0.0166(3)	0.0013(3)
Ni		0.0188(7)	0.0110(6)	0.0169(6)	-0.0042(4)
*M***		0.0168(6)	0.0105(5)	0.0136(5)	0.0020(3)

*M = 0.59(5) Ga + 0.41(5); **M = 0.15(2) In + 0.85(2) Ga; $U_{12} = U_{23} = 0$

Table 3

Interatomic distances in the structures of $YNi_{0.83}Ga_{1.17}$ and $YNiIn_{0.15}Ga_{0.85}$

Atom		δ, nm	CN	Atom		δ, nm	CN
			$YNi_{0.83}Ga_{1.17}$				
Y	2*M*	0.2979(1)	16	*M**	2*M*	0.2486(1)	12
	4*M*	0.2981(1)			*M*	0.2545(1)	
	2*M*	0.3122(1)			*M*	0.2672(1)	
	4*M*	0.3136(1)			Y	0.2979(1)	
	2Y	0.3531(1)			2Y	0.2981(1)	
	2Y	0.3643(1)			Y	0.3122(1)	
					2Y	0.3136(1)	
					2*M*	0.3649(1)	
			$YNiIn_{0.15}Ga_{0.85}$				
Y	Ni	0.2897(2)	16	Ni	2*M*	0.2517(1)	10
	2Ni	0.2986(1)			*M*	0.2560(2)	
	2*M*	0.3032(1)			*M*	0.2694(2)	
	M	0.3054(1)			Y	0.2897(2)	
	M	0.3099(1)			2Y	0.2986(1)	
	2Ni	0.3123(1)			2Y	0.3123(1)	
	2*M*	0.3160(1)			Y	0.3307(2)	
	Ni	0.3307(2)		*M***	2Ni	0.2517(1)	10
	2Y	0.3549(2)			Ni	0.2560(2)	
	2Y	0.3663(1)			Ni	0.2694(2)	
					2Y	0.3032(1)	
					2Y	0.3054(1)	
					Y	0.3099(1)	
					2Y	0.3160(1)	

*M = 0.59(5) Ga + 0.41(5); **M = 0.15(2) In + 0.85(2) Ga

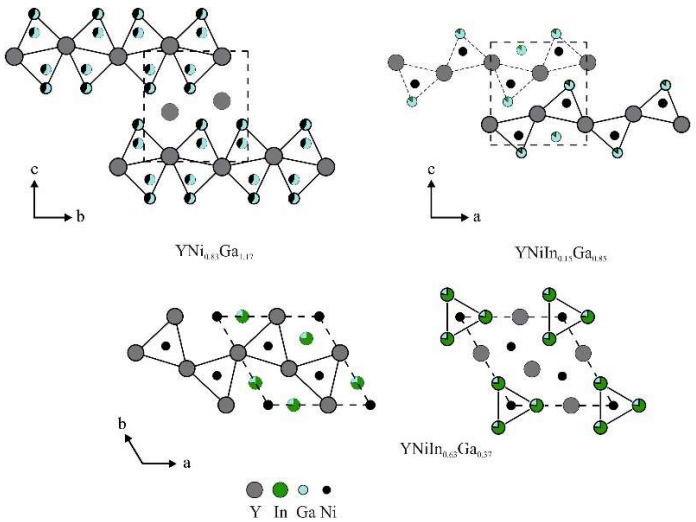

Fig. 1. Stacking of the trigonal prisms in the structures of: $YNi_{0.83}Ga_{1.17}$, $YNiIn_{0.15}Ga_{0.85}$ and $YNiIn_{0.63}Ga_{0.37}$ [5].

Trigonal prisms of yttrium atoms in the $YNiIn_{0.63}Ga_{0.37}$ compound are connected by shared edges and form chains along the direction *a*. We observed the formation of two similar chains of trigonal prisms on a different hight in $YNiIn_{0.15}Ga_{0.85}$ structure. Trigonal prisms are connected by shared rectangular faces and form chains along direction *b* in $YNi_{0.83}Ga_{1.17}$ compound with KHg_2-type structure. Atoms of the *p*-elements (or atoms of the statistical mixture) are located in the vertices of one of the edges of trigonal prisms, and the other vertices are occupied by yttrium atoms in $YNi_{0.83}Ga_{1.17}$ (KHg_2) and $YNiIn_{0.15}Ga_{0.85}$ (HoNiGa) structures. Whereas, in the $YNiIn_{0.63}Ga_{0.37}$ (ZrNiAl) structure two types of prisms can be separated: some are formed exclusively by atoms of yttrium and others – by atoms of *p*- (or atoms of statistical mixture). Substitution the atoms of *d*- or *p*-elements by the atoms of *p*-elements in structures of these compounds occurs in the positions of atoms that form the trigonal prisms.

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REFERENCES

1. *Chumalo N., Demchuk V., Nychyporuk G., Zaremba V.* Investigation of the interaction of the components in $R_2T_2In_{1-x}M_x$ (*R* = La, Ce; *T* = Ni, Cu; M = Al, Sn; $0 \le x \le 1$) systems. Visn. Lviv Univ. Series Chem. 2010. Vol. 51(1). P. 24–30 (in Ukrainian).
2. *Dominyuk N., Nychyporuk G., Muts I., Pöttgen R., Zaremba V.* Solubility of *p*-elements III and IV groups in the Gd_2Cu_2In compound. Visn. Lviv Univ. Series Chem. 2013. Vol. 54. P. 57–63 (in Ukrainian).
3. *Kharkhalis A., Horiacha M., Nychyporuk G., Bednarchuk O., Zaremba V.* Investigation of interaction of the components in $RECu_2In_{1-x}Al_x$ (*RE* = Y, La, Gd) systems. Visn. Lviv Univ. Series Chem. 2014. Vol. 55(1). P. 54–62 (in Ukrainian).
4. *Horiacha M., Zinko L., Nychyporuk G., Serkiz R., Zaremba V.* The $GdTIn_{1-x}M_x$ (*T* = Ni, Cu; *M* = Al, Ga; $0<x<1$) systems. Visn. Lviv Univ. Series Chem. 2017. Vol. 58(1). P. 77–85 (in Ukrainian).
5. *Horiacha M., Savchuk I., Nychyporuk G., Serkiz R., Zaremba V.* $YNiIn_{1-x}M_x$ (*M*= Al, Ga, Sb) systems. Visn. Lviv Univ. Series Chem. 2018. Vol. 59(1). P. 67–75 (in Ukrainian). (https://doi.org/10.30970/vch.5901.067).
6. *Horiacha M., Rinylo N., Nychyporuk G., Serkiz R., Pöttgen R., Zaremba V.* The interaction of the components in $YCuIn_{1-x}M_x$ (*M* = Al, Ga) systems. Ukr. Chem. Journal. 2018. Vol. 84(11). P. 31–37 (in Ukrainian).
7. *Zaremba N., Nychyporuk G., Schepilov Yu., Panakhyd O., Muts I., Hlukhyy V., Pavlyuk V.* The $CeNiIn_{1-x}M_x$ (*M* = Al, Ga) systems at 873 K. Ukr. Chem. Journal. 2018. Vol. 84(12). P. 76–84 (in Ukrainian).
8. *Zaremba N., Nychyporuk G., Schepilov Yu., Serkiz R., Hlukhyy V., Pavlyuk V.* The interaction of the components in the $CeNiIn_{1-x}M_x$ (*M* = Ge, Sb) systems. Visn. Lviv Univ. Series Chem. 2019. Vol. 60(1). P. 82–90 (in Ukrainian). (https://doi.org/10.30970/vch.6001.082).
9. *Klicpera M., Javorský P., Šantava E.* Magnetic phase transitions in TbNi(Al,In) compounds. Acta Phys. Polonica A. 2010. Vol. 118(5). P. 881–883. (https://doi.org/10.12693/APhysPolA.118.881).
10. *Godnek Ł., Żukowski J., Bałanda M., Kaczorowski D., Szytuła A.* Magnetism and electronic structures of hexagonal 1:1:1 rare earth-based intermetallic compounds. Materials Science-Poland. 2008. Vol. 26(4). P. 815–820.

11. *Gupta S., Suresh K. G.* Review on magnetic and related properties of RTX compounds. J. Alloys Compd. 2015. Vol. 618. P. 562–606 (https://doi.org/10.1016/j.jallcom.2014.08.079).
12. *Brtick E., De Boer F.R., Nozarh P., Sechovsky V., Havela L., Buschow K.H.J., Andreev A.V.* Influence of Y, Fe and Co substitutions on electronic properties of UNiAl. Physica B. 1990. Vol. 163. P. 379–381. (https://doi.org/10.1016/0921-4526(90)90217-I).
13. *Rayaprol S., Heying B., Pöttgen R.* The Solid Solution $CeAuIn_{1-x}Mg_x$ – Structure, Magnetic Properties and Specific Heat Data. Z. Naturforsch. 2006. Vol. 61B. P. 495–502. (https://doi.org/10.1515/znb-2006-0501).
14. *Ehlers G., Ahlert D., Ritter C., Miekeley W., Maletta H.* Anomalous transition from antiferromagnetic to ferromagnetic order in the pseudoternary series $TbNi_{1-x}Cu_xAl$. Europhys. Lett. 1997. Vol. 37(4). P. 269–274 (https://doi.org/10.1209/epl/i1997-00142-5).
15. *Zarzycki A., Szytuła A.* Magnetic properties of $Tb_{1-x}Y_xNiIn$ system. Acta Phys. Polonica A. 2012. Vol. 122(2). P. 382–383 (https://doi.org/10.12693/APhysPolA.122.382).
16. *Bałanda M., Penc B., Baran S. et al.* Magnetic Properties of $TbNi_{1-x}Au_xIn$ Compounds. Acta Phys. Polonica A. 2009. Vol. 115(1). P. 174–177 (https://doi.org/10.12693/APhysPolA.115.174).
17. *Dwight A.E., Mueller M.H., Conner R.A. Jr., Downey J.W., Knott H.W.* Ternary compounds with the Fe_2P-type structure. Trans. Metall. Soc. AIME. 1968. Vol. 242. P. 2075–2080.
18. *Yarmolyuk Y.P., Grin Y., Gladyshevskii E.I.* The crystal structure of RGaNi compounds (R = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). Dopov. Akad. Nauk Ukr. RSR, Ser. A 1979. No 9. P. 771–775.
19. *Vasilechko L.O., Grin Yu., Fedorchuk A.O.* New ternary gallides with the KHg_2 and $CaIn_2$ structures. Inorg. Mater. 1994. Vol. 30(11). P. 1409–1411. (in Russian).
20. *Ferro R., Marazza R., Rambaldi G.* Equiatomic Ternary Phases in the Alloys of the Rare Earths with Indium and Nickel or Palladium. Z. Metallkd. 1974. Vol. 65. P. 37–39.
21. *Petříček V., Dušek M., Palatinus L.* Crystallographic Computing System JANA 2006: General features. Z. Kristalogr. 2014. Vol. 229(5). P. 345–352 (https://doi.org//10.1515/zkri-2014–1737).
22. *Emsley J.* The Elements: 2nd ed. Oxford: Clarendon Press, 1991. 251 p.
23. *Krypyakevych P.I.* Structure types of the intermetallic compounds. M.: Nauka. 1977. 290 p. (in Russian).

РЕЗЮМЕ

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КРИСТАЛІЧНА СТРУКТУРА СПОЛУК $YNi_{0,83}Ga_{1,17}$ І $YNiIn_{0,15}Ga_{0,85}$

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Кристалічну структуру сполук $YNi_{0,83}Ga_{1,17}$ (структурний тип KHg_2, просторова група *Imma*, a = 0,43006(4), b = 0,69108(6), c = 0,73371(6) нм, R_1 = 0,0315, wR_2 = 0,0635) і $YNiIn_{0,15}Ga_{0,85}$ (структурний тип HoNiGa, просторова група *Pnma*, a = 0,69313(5), b = 0,43225(7), c = 0,74315(9) нм, R_1 = 0,0777, wR_2 = 0,0658) уточнено методом монокристала. Для отримання монокристалів зразки складу YNiGa та $YNiIn_{0,2}Ga_{0,8}$ синтезовано методом електродугової плавки, піддано спеціальній термічній обробці та досліджено рентгенівським методом (автодифрактометр Stoe IPDS II, MoKα-випромінювання). Якісний

та кількісний склад досліджених монокристалів підтверджено результатами EDX аналізу (скануючий електронний мікроскоп Zeiss EVO MA10). Кристалічні структури сполук системи $YNiIn_{1-x}Ga_x$ належать до класу сполук з тригонально-призматичною координацією атомів меншого розміру. У структурі сполуки $YNiIn_{0,63}Ga_{0,37}$ (структурний тип ZrNiAl) тригональні призми, утворені атомами ітрію і з'єднані спільними ребрами, утворюють ланцюги вздовж напрямку *a*. Формування двох подібних ланцюгів на різних висотах простежується в структурі сполуки $YNiIn_{0,15}Ga_{0,85}$ (структурний тип HoNiGa). У структурі сполуки $YNi_{0,83}Ga_{1,17}$ (структурний тип KHg_2) тригональні призми, з'єднані спільною прямокутною гранню, утворюють ланцюги вздовж напрямку *b*. Атоми *p*-елементів (або атоми статистичної суміші) розташовані у вершинах одного з ребер тригональних призм, а решта вершин зайняті атомами ітрію у структурах сполук $YNi_{0,83}Ga_{1,17}$ і $YNiIn_{0,15}Ga_{0,85}$. Тоді як, у структурі сполуки $YNiIn_{0,63}Ga_{0,37}$ можна виділити два типи призм: одні утворені виключно атомами ітрію а інші – атомами *p*-елементів (або атомами статистичної суміші). Заміщення атомів *d*- або *p*-елементів атомами *p*-елементів у структурах цих сполук відбувається в положеннях, що утворюють тригональні призми.

Ключові слова: галій, індій, метод монокристала, кристалічна структура.

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